

Docket No.: 1155-0214P  
(PATENT)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of:  
Mamoru TAKAHASHI et al.

Application No.: 09/744,904

Confirmation No.: 8530

Filed: January 31, 2001

Art Unit: 1713

For: ETHYLENE (CO)POLYMERS AND USES  
THEREOF

Examiner: R. A. Lee

**DECLARATION UNDER 37 C.F.R. 1.132**

MS AF  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Naoto MATSUKAWA, declare the following:

I received my degree of M.A. in 1997 from Okayama University, Faculty of Engineering,  
Department of Applied Chemistry.

I joined Mitsui Petrochemical Industries (now Mitsui Chemicals, Inc.) in 1997.

Since 1998, I have been an olefin polymerization catalysis researcher at Sodegaura  
research center.

I am one of the inventors of the present invention.

I have read and understand the Office Action dated March 23, 2007 and the reference  
cited therein to Malmberg et al. (Macromolecules, 1998, Vol. 31, pages 8448-8454).

Currently, claim 1 recites that the inventive ethylene (co) polymer (A1) which is either  
an ethylene homopolymer or a copolymer of ethylene and an  $\alpha$ -olefin of 4 to 20 carbon atoms,  
comprises the following Features: (iv<sub>A1</sub>)<sup>1</sup> the number of branches having a length equivalent to

<sup>1</sup> I use herein, the numbering of the Features as used in the claims.

that of hexyl or longer measured by  $^{13}\text{C}$ -NMR is less than 0.1 per 1,000 of carbon atoms, and ( $v_{A1}$ ) the intrinsic viscosity  $[\eta]$  in dl/g measured at 135°C in decalin and the melt flow rate MFR in g/10 minutes measured under 2.16 kg load at 190°C satisfy the following relations:

$$[\eta] > 1.85 \times \text{MFR}^{0.192} \text{ when MFR} < 1, \text{ and}$$

$$[\eta] > 1.85 \times \text{MFR}^{0.213} \text{ when MFR} \geq 1.$$

I have performed the following experiment(s) to determine that none of the polymers of Malmberg et al. have this combination of Features ( $iv_{A1}$ ) and ( $v_{A1}$ ).

Sample B5 is discussed at page 8450, 2<sup>nd</sup> column, lines 5-6 from bottom of Malmberg et al., and is the only example wherein the amount of branching is described. Accordingly, it is my opinion that only Sample B5 of Malmberg et al. could meet the branching Feature ( $iv_{A1}$ ) of claim 1.

I now describe the process I used for repeating Sample B5 of Malmberg et al. and report that Sample B5 does not meet the MFR and intrinsic viscosity  $[\eta]$  relationship described in Feature ( $v_{A1}$ ) of claim 1. The experiments disclosed herein were performed by me or under my direct supervision.

Sample B5 disclosed in Malmberg et al. has been essentially repeated according to the description of Malmberg et al, which is as follows:

#### Experimental Section

Polymerization method: solution polymerization

Solvent: Toluene 800ml

Ethylene partial pressure: 1 bar

Catalyst: Ethylene bis indenyl zirconium dichloride (Not supported, dissolved in Toluene)

Co-catalyst: Methyl Alumoxane (MAO)

Comonomer: none

Hydrogen: not added

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**Table 1 : Polymerization conditions**

Sample	Catalyst: mM	Co- catalyst: mM	Ethylene Flow rate: L/hr	Polymerization Temperature:	Polymerization Time: min.	Yield: g
Run #1	0.0008	4.0	100	80	5	6.51
Run #2	0.0008	4.0	100	80	5	6.84

**Table 2 : Physical Properties Of Polymer Obtained**

Sample	Mn	Mw	Mw/Mn	$[\eta]$ : dg/l	MFR	*1
Run #1	$3.32 \times 10^4$	$6.68 \times 10^4$	2.0	1.44	1.70	1.652
Run #2	$3.45 \times 10^4$	$6.87 \times 10^4$	2.0	1.52	1.09	1.816

\*1 =  $1.85 \times \text{MFR}^{0.213}$ **Condition of GPC measurement**

Equipment: Gel Permeation Chromatograph, Product of Waters Corporation  
Alliance GPC 2000 series

Measurement condition:

Column: Product of Tosoh Corporation

TSKgel GMH6-HTX2 + TSKgel GMH6-HTX2

(Column size: 7.5 mm I.D. x 30 mm)

Column Temperature: 140°C

Mobile phase: o-dichlorobenzene [containing 0.025% of BHT (Butyl Hydroxy Toluene)]

Detector: differential refractometer

Flow rate: 1 mL/min.

Concentration at testing: 0.15% (W/V)

Injection volume: 500  $\mu$ L

Time interval of sampling: 1 sec.

Calibration sample: mono-dispersed polystyrene (product of Tosoh Corporation)

**Condition of MFR measurement**

2.16 Kg load at 190°C

**Condition of  $[\eta]$  measurement**

Measured in decalin at 135°C

### Comments/Conclusions Based on Experimental Results

As shown in Table 2, the MFR and intrinsic viscosity  $[\eta]$  relationship described in Feature (v<sub>A1</sub>) of claim 1 is not satisfied, i.e., Sample B5 of Malmberg et al. does not meet the requirement of  $[\eta] > 1.85 \times \text{MFR}^{-0.213}$  when  $\text{MFR} \geq 1$ .

I am aware that the polymerization time used herein is different from that described for the sample disclosed in Malmberg et al. Specifically, the polymerization time of the experiment (5 minutes) is different from that of Malmberg et al. (60 minutes). However, for the following technical reasons, it is my opinion that the difference in polymerization time would not significantly affect the ratio of intrinsic viscosity  $[\eta]$  and  $\text{MFR}^{-0.213}$ .

The polymer of Malmberg et al. is obtained by polymerizing olefins using a metallocene catalyst. The mechanism of the olefin polymerization is called an addition polymerization. The mechanism is described in "Chemistry of polymer synthesis," revised version (published by KAGAKUDOJIN in March 1, 1989, 11th impression of the second edition), a copy of which is attached hereto for the Examiner's convenience. The relevant part (pages 33 to 34) of which is translated to English as follows.

Among these reactions addition polymerization and polycondensation have been studied from long ago, and it is believed that addition polymerization and polycondensation proceed with chain reaction and stepwise reaction, respectively. ...

Chain reaction and stepwise reaction have essentially different polymerization mechanisms.

Generally, chain reaction comprise following 4 primary reactions;  
initiation that generates unstable chain carrier,  
propagation in which chain carrier react in cascade,  
termination in which propagation is terminated, and chain transfer reaction.

Supposing that M stands for monomer, P stands for polymer, and A stands for substance that can cause chain transfer reaction; each reaction can be described as follows:

Initiation:	$M \rightarrow M^*$
Propagation:	$M_n \rightarrow M_n^*$
Termination:	$M_n \rightarrow P$
Chain transfer:	$M_n^* + A \rightarrow P + A^*$

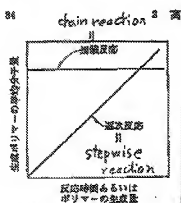
wherein  $M_n^*$  is the chain carrier and any of radical, anion or cation. Among these primary reactions, Initiation is the slowest one, and once a chain carrier is generated, propagation occurs immediately.

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Generally, when polymerization proceeds with chain reaction, average molecular weight of the resultant polymer is constant as in figure 2-1, regardless of time of reaction. To the contrary, in stepwise reaction functional group react consecutively to form polymer. There are no unstable intermediates such as chain carrier in the reaction, and average molecular weight of the polymer increase with time of reaction as in figure 2-1.

Figure 2-1



[caption]

Relation between average molecular weight of the polymer and time of reaction for chain reaction and stepwise reaction

[Y-axis]

average molecular weight of polymer

[X-axis]

time of polymerization reaction

This teaching can be summarized follows.

With respect to polymerization, there are chain reactions and stepwise reactions. In the case of addition polymerization, the reaction proceeds with chain reaction. The average molecular weight is constant regardless of polymerization time.

So the polymer properties such as MFR and intrinsic viscosity, which are closely related to the molecular weight of a polymer, are not expected to change with time. As such, it is my opinion that the difference in polymerization time between Sample B5 of Malmberg et al. and the polymerization time reported herein would not significantly affect the ratio of intrinsic viscosity  $[\eta]$  and MFR<sup>0.213</sup>.

In a *separate matter*, the Examiner expressed during the recent Interview with my representative, Dr. Dahlen, that the ratio of catalyst to cocatalyst is an important variable. The Examiner is aware that Malmberg et al. do not disclose the ratio of catalyst/cocatalyst. The Examiner is concerned that the catalyst/cocatalyst ratio affects the MFR and intrinsic viscosity  $[\eta]$  of the Sample B5. I respectfully disagree with the Examiner.

First, if the ratio of catalyst/co-catalyst greatly affects the properties of the polymer produced, then it makes sense that Malmberg et al. have not placed into possession of the public the polymer of Sample B5. In other words, based on this logic, if the ratio is not disclosed, then Sample B5 of Malmberg et al. could not be reproduced.

Second, I conducted the experiments to show that Sample B5 does not satisfy the equation regarding MFR and  $[\eta]$  of the present claim, believing that the effect of the co-catalyst/catalyst ratio is small. It is my opinion that the experiments described herein are sufficient to show that the Sample B5 does not satisfy the relation of the claim regarding MFR and  $[\eta]$ .

It is my opinion that since the polymerization conditions are not disclosed in Malmberg et al., it is logical to assume that the polymerization conditions are in the normal range that one skilled in the art would select. As such, there is not a big difference between the polymerization conditions of the experiments described herein and that of Malmberg et al.

In conclusion, it is my opinion that none of the polymers of Malmberg et al. have the inventive combination of Features (iv<sub>A1</sub>) and (v<sub>A1</sub>).

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: August 21, 2007By: Naoto Matsukawa  
Naoto Matsukawa

Attached: "Chemistry of polymer synthesis," revised version (published by KAGAKUDOJIN in March 1, 1989, 11th impression of the second edition).



改訂高分子合成の化学

大 隈 隆 行 著

化学同人



## 2.3 高分子合成反応の分類と特徴

触媒や溶媒や脱水素を要しなから重合する場合であり、水やアルコールなどが触媒する重合と機械的に異なる点が多い。本書では区別して取り扱うことにする。

このなかで、付加重合および連鎖反応はよくから詳しく研究され、それぞれ連鎖反応(chain reaction)および逐次反応(stepwise reaction)で述べられている。そのほかの反応は明らかでない場合もあるが、1~4は連鎖反応で、5~8は逐次反応で述べられている。

連鎖反応ならびに逐次反応による高分子の生成反応は、本質的に真な特徴を示す(表 2-3 参照)。一般に、連鎖反応は次の四つの要素からなっている。すなわち、不安定な連鎖でい伝体(chain carrier)のできる開始反応(initiation)、それが次々に反応を起す生長反応(propagation)、それが停止する停止反応(termination)、およびそれが他の物質に移動する連鎖移動反応(chain transfer reaction)である。

いま、Mをモノマー、Pをポリマー、Aを連鎖移動反応を起こすような物質とすると、次のように表ける。

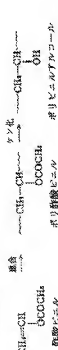


ここで、M<sup>\*</sup>は連鎖でい伝体で、ラジカル、カチオン、アニオンの3種類がある。ラジカルを生成して進む重合では、これら3種類のうちで、開始反応が最も起こりやすく、一度連鎖でい伝体が生成するとときわめてすみやかに生長する。一般に、連鎖重合で進む場合は図2-1に示すように生成ポリマーの平均分子量は反応時間に比例して一定である\*。

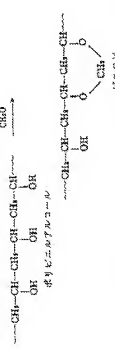
\* 図2-1の図解はラジカル重合で、しかも最も初期の段階で成立する。数滴がかりで進行した場合、そのうちで最も成立しない(分子間が增大)場合がある。また、ラジカル重合では分子量は重合率とともに増大する。

## 2 重合分子の生成

集合によって生成するはずであるが、ビニルアルコールは実在しない(アセトアルデヒド異性体として存在する)。したがって、次のように断鎖ビニルを重合してポリ断鎖ビニルをつくり、ついでケン化することによって初めて合成される。



また、ビニオン機構はポリビニルアルコール系にアルムアルデヒドを反応させ、部分的にアルマール化したものである。



このように高分子の化学反応によっても、多くの重要な高分子が合成され、また高分子の性質の改善(改質)が行われている(4章参照)。

## 2.3 高分子合成反応の分類と特徴

以上に述べた実験から、高分子から高分子を合成する反応を分類すると次のようになる。

1. 付加重合(値付)
2. 縮合重合
3. 異性化重合
4. 断鎖重合
5. 断鎖重合
6. 変性重合
7. 重合
8. 付加重合

この分類は、断鎖重合を除いては多くの事例にみられる分類と同じである。ここでいう断鎖重合は、断鎖化反応による断鎖化反応を伴って断



一方、逐次反応では官能基が逐次に反応を繰り返して高分子化してゆく。したがって、反応の途中に連鎖といふ体のような不安定な中間体は生成せず、生息ポリマーの平均分子量は、図2-1のように反応時間と共に増大する。

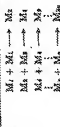


図2-1 連鎖反応あるいは逐次反応における反応時間と平均分子量の関係(いずれも反応初期を示したもので反応後期には増大する)

連鎖反応および逐次反応による高分子化反応の典型的な違いを表2-2にまとめると、

表2-2 連鎖反応と逐次反応による高分子化反応の比較

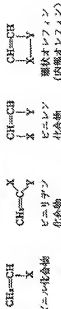
連鎖反応による高分子化(付加重合)	逐次反応による高分子化(重縮合)
生長は連鎖的(低体とモノマーの反応で起こり、連鎖的(低体と密着に反応する)物知なく、1官能基の化合物を加えると分子量は低下する。	モノマー濃度の低いポリマー中の官能基は、反応の途中で増大する。モノマー濃度は1%以下となる。
モノマー濃度は反応を進めて減少し、反応の途中で増大する。モノマー濃度は1%以下となる。	モノマー濃度は反応を進めて減少し、反応の途中で増大する。モノマー濃度は1%以下となる。
高分子量のポリマーがたがいに生成し、反応の進行と共に分子量は増加して変化する(図2-1)。	分子量のポリマーの増加と共に増大(図2-1)。

## 2.4 ビニル化合物の重合

### 2.4.1 ビニル化合物の重合の形式

炭素-炭素二重結合を有する化合物は、それと結合した置換基の数と付加によって次のようによばれる。

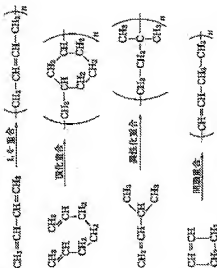
### 2.4 ビニル化合物の重合



このうち、断続重合するモノマーは主としてビニルとビニル化合物であるので、このような化合物を断続してビニルモノマー (vinyl monomer) と区別せずによばれることがある。これらの化合物は、それぞれ重合のしやすさは異なるが、一般に、二重結合が環に隣りて付加重合する。



このような重合の形式はビニル重合 (vinyl polymerization) とよばれる。ただし、ある種のビニルモノマーでは上述のビニル重合と同時に、次のような形式の重合が起こる。



このうち、共役ジエンの1,4-重合を断続重合といっていることは、ビニル重合は連鎖反応で進むので、連鎖的(低体)がラジカルであるか、カチオンであるか、アニオンであるかによって、それぞれラジカル重合 (radical polymerization), カチオン重合 (cationic polymerization), あ

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環鎖反応による高分子合成反応

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## 改訂高分子合成の化学

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